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The CSP/PSR approach in reduced chemistry of premixed ammonia combustion

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Abstract

In order to fire gas turbine engines on ammonia, knowledge is acquired about the combustion characteristics and model possibilities of this carbon free fuel. To this end in this paper the projection of detailed chemistry of ammonia on a low dimensional chemistry model is investigated at atmospheric pressure and temperature conditions. On basis of this turbulent combustion models for ammonia can developed on basis of available modeling procedures for hydrocarbon combustion. These turbulent combustion models are based on a projection of the high dimensional detailed chemistry on a single dimension reaction progress variable. This work describes a methodology to define an optimal expression of the reaction progress variable in the context of tabulated chemistry on basis of laminar premixed combustion. Two methods are used: the Computational Singular Perturbation (CSP) method and a sensitivity analysis of the time scales evaluated with a Perfectly Stirred Reactor (PSR). The thermo-chemical databases computed with these techniques are compared in the cases of a freely propagating flame, in the laminar premixed regime and under stoichiometric conditions. The accuracy of the chemical projection is evaluated on basis of a comparison of predicted species concentration and temperature profiles in a freely propagating flame based on detailed chemistry and the single reaction progress variable. It is found that the projection is very accurate and hence the combustion of ammonia can be predicted on basis of one dimensional tabulated chemistry.

Keywords: ammonia;tabulated chemistry;reaction progress variable;combustion

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1. Introduction

The target in this paper is to apply all the expertise and tools developed for natural gas combustion for modeling of NH3 combustion. This is interesting in view of the large differences in characteristics between natural gas and NH3 as a fuel. The main reason to choose NH3 over natural gas is of course that NH3 has a carbon free foot print. For combustor design purposes numerical analysis is important. The modeling of turbulent combustion with detailed chemistry is however difficult. This can be resolved by introducing tabulated chemistry. In this context, a thermochemical database is built and parametrized in terms of a number of controlling variables. Transport equations of these variables are solved during the combustion simulations and the thermal-transport properties, as well as the source terms, are retrieved from the pre-computed database. The variable describing the state of the reaction is called reaction progress variable, "c", which in premixed adiabatic flames is the only control variable. In this work, a methodology to find a best definition of c for ammonia combustion is followed, as previously successfully used for methane and ethanol combustion (Fratalocchi and Kok 2017). A crucial part of modeling the combustion process is the ability to resolve the meaningful chemical time scales. An algorithm designed to select the slow and the fast time scales is the Computational Singular Perturbation (CSP) method, proposed by Goussis et al. (1990), and further elaborated by Lu et al. (2001) for methane oxidation. For the modeling of ammonia combustion in this paper the criterion to analyse the characteristic chemical time scales as proposed by Lu et al. (2001), is compared with the CSP method in a Perfectly Stirred Reactor, with the PSR package from Chemkin-II (Kee et al. (1989)). In a PSR environment, the reference time is given by the extinction time and the chemical time scale is chosen to be the consumption of molar concentration of the species. In this context, it is possible to define a threshold value to separate the space of the species between slow and steady state species. To assess the influence of the definition of c, the tabulations are validated against a freely propagating laminar premixed flame. Predictions of the laminar burning flame, as well as species mass fractions and temperature profiles, are compared with those obtained with detailed chemistry in Chemkin. The simulations, all in steady state and based on tabulated chemistry, are carried out with the commercial software CFX Ansys. For the simulated test-case, the thermochemical database with tabulated chemistry is implemented in CFX and looked up at each iteration through an user-defined Fortran routine.

2. Chemical reacting system

The temporal evolution of species mass fractions of a reacting flow is determined by convection, diffusion and chemical reaction with reaction rate ω_n of the species n. The full set of equations is described in detail in Williams (1985). Our focus is on projection of the transport of all species 1 to N on one progress variable for the ammonia chemical reaction system. The transport of a species with mass fraction Y_n is described by the equation:

$$\frac{\partial \rho Y_n}{\partial t} + \frac{\partial (\rho u_i Y_n)}{\partial x_i} = -\frac{\partial}{\partial x_i}\left((\rho D \frac{\partial Y_n}{\partial x_i}) \right) + \dot{\omega}_n \qquad n=1,..,N \tag{1}$$

Unity Lewis number is assumed. For the reaction rate of each n_{th} species, all the elementary reactions involved are taken into account. To determine these rates a conversion needs to be made to mole fractions of each species. These reaction rates are characterized by a wide range of time scales. Each species evolves with its own rate, and the global reaction involves both slow and fast processes. Equation (2) describes in terms of the mole fraction X_n of a species the time scale of the change of the concentration of a species. A fast reaction corresponds to a small chemical time scale. Generally in a chemical kinetic system, the range of rates is spread over several orders of magnitude. This is investigated in the case of a homogeneous reactor, where a characteristic time is chosen to divide the space of the species into fast and slow domains.

$$\tau_{chem,n} = \frac{[X_n]}{d[X_n]/dt} \qquad n=1,..,N \tag{2}$$

3. CSP algorithm

The Computational Singular Perturbation algorithm is used to reduce large detailed kinetic mechanisms. The derivation of reduced mechanisms is based on the concept that the evolution in time of a reacting system is driven by a small number of reaction rates. This is because after an initial transient time, some of the species reach an invariant state, called steady-state. The CSP algorithm identifies the steady-state species and the fastest elementary rates associated with them; the reduced mechanism is then created by removing those species from the original detailed scheme. An extensive description of the CSP method can be found elsewhere (Massias et al. (1999). The slow time scales are rate determining for the chemical process, and any perturbation caused by the M species production or destruction rate can be neglected. The fast species are exactly the ones identified by the so-called CSP pointers. With the help of the pointers a composed mass fraction can be determined on basis of weighted (b^c vector) summation over all species reactions such that the source term does not have a contribution of the fast species source terms.
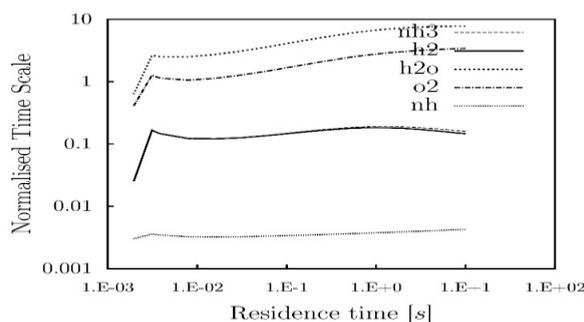
4. Analysis of chemical time scales

Fig. 1. Normalized time scale of major species reactions as a function of PSR residence time.

The characteristic chemical time scale describing the consumption rate of the species involved in a reaction is expressed by eq. (2). When τ_{chem_n} is small compared to a reference time in the reactor or across a laminar flame, the corresponding reaction is in equilibrium and the species can be seen in steady state. Referring to previous work from Lu et al. (2001), a homogeneous reacting system is chosen to identify the characteristic chemical time scales of the species. This implies that only the chemical properties of the mixture are taken into account. A set of simulations is run in the Perfectly Stirred Reactor (PSR) with the objective of selecting the fast and slow species. This was done for NH3 perfectly premixed in stoichiometric ratio with air at 1 bar and 288 K. At each simulation, the residence time is manually decreased to identify the extinction time. The maximum residence time is representative of the equilibrium conditions. In a laminar flame the species concentrations evolve along a spatial coordinate. But in the case of a homogeneous system, like the PSR, the species concentrations are just a function of the residence time. The variables evaluated are: the chemical time scales of the species and a reference characteristic time for the evolution of the reaction, that is subsequently used to normalize the calculated specie's chemical time scales. As a reference time in the PSR is chosen the extinction time. The extinction time is defined as the minimum residence time, τ_{res}, for which the reactions can take place under specific initial conditions. In fig. 1 the normalized time is plotted against a range of residence time for some major species (NH3, H2, H2O, O2 and NH). The reaction reaches equilibrium conditions at residence time of 10s as can be concluded from the tail of the curves. The best candidates for steady state species are those associated with the smaller chemical time scales, for example NH and H2O. Normalized time scales of fast and slow minor species (OH, HNO, N2O and NH2) as well as major species N2 are shown in fig. 2(a). It is clear that the time scales of the radicals OH and NH2 are 2 orders of magnitude shorter than the major species N2O, N2, O2 and H2.
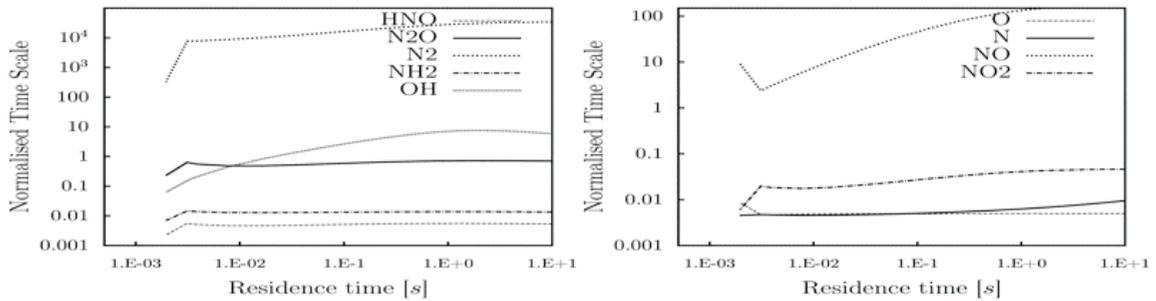
Fig. 2. (a) Normalized time scale of minor species reactions as a function of PSR residence time; (b) Normalized time scale of nitric oxide species reactions as a function of PSR residence time.

Since ammonia has fuel bound nitrogen normalized time scales of NO, NO2, N and O are depicted as a function of residence time in figure 2(b). It can be observed that the time scales of the radicals N and O and of NO2 are very small and can be identified as fast species. The time scale of NO is 3 orders of magnitude larger and can be identified to be a slow species in the process of ammonia combustion. This means that NO production proceeds on a much larger time scale than ammonia consumption. In figures 1 and 2 it can be seen that time scales do not change anymore after the residence time reaches value of 10s, with the exception of NO. This means that all species reach equilibrium values within 10 s, except for NO.

5. One-dimensional laminar database

Using the information on slow and fast species and the CSP output the detailed chemical reaction system can be projected on a reduced manifold with at least one controlling reaction progress variable. A composed species that describes reaction progress is now defined by eqs 3 and 4:

$$\eta^i = \sum_{k=1}^{N} b_k^i \frac{W}{W_k} Y_k \tag{3}$$

$$c = \frac{\eta - \eta_u}{\eta_b - \eta_u} \tag{4}$$

where the CSP base b^i vectors are weighted in terms of mass with W being the mean molecular weight of the mixture, and W_k the molecular weight of the k-th species. The reaction progress variable c can be written as in eq 4. The reacting domain is covered from the unburnt side c=0, towards the burnt region c=1. A comparison of tabulations is made below between the b-vector obtained with the CSP method, b_{csp}, and a user defined combinations of species mass fractions with weight 1 for selected species and 0 for the others. The question is how to choose this set of weight factors for the species (when the automatic procedure of CSP is not used). It appears that the species which are in
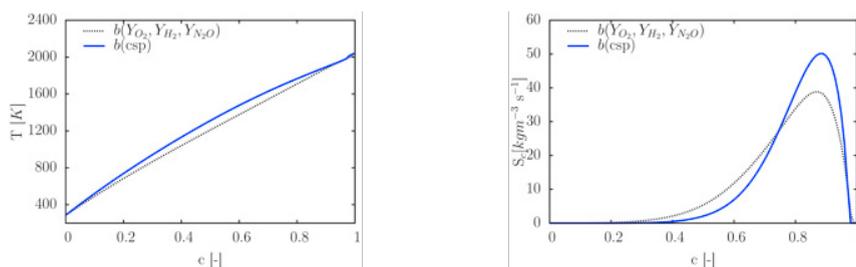

Fig. 3. (a) Temperature as a function of reaction progress; (b) C source term as a function of c.

the range close to unity of the normalized time scale are the most suitable to represent the evolution of the reaction system. These are O2, H2, N2O. In fig 3(a) the reacting gas temperature obtained with the time scale based manual definition of the b-vector and b_{csp} is plotted. Both definitions of b give a very similar profile of the temperature, which is almost linearly increasing with the reaction progress variable. This linear profile is exactly what the projection was aimed at. The source term of the reaction progress variable as a function of progress is shown in fig.3(b). The CSP and the manual choice based reaction progress variable give very similar results. The source term is zero at c=0 and c=1, which is a requirement, and with c increasing from 0 the source term slowly increases to a maximum at about c=0.85 and reduces to 0 subsequently. As stated in Goevert et al. (2015) for a turbulent CH4~air flame, a less steep curvature of the source term is beneficial when assumed shape PDF-integration is used. Both b-vectors show here a similar curvature. Important conclusion is that the projection of ammonia chemistry from a detailed reaction mechanism on a one dimensional manifold is very well possible. The time scale based slow variable selection with unity weight factors is performing as well as the mathematical CSP method. For both definitions of b and the reaction progress variables, a tabulated database is built for laminar premixed ammonia/air combustion. The built look-up database is retrieved at each iteration by the solver in solving the transport equation of the reaction progress variable. The tabulation is made by mapping all the properties over an equidistant grid of c, made of 100 points.

6. Freely propagating flame

The calculated one-dimensional database is tested imbedded in CFX against the solution of a 1D freely propagating flame obtained with Chemkin Premix. A stoichiometric mixture of air and ammonia burns at pressure 1 bara and T_{inlet} 288 K. The 1D laminar database described in section 5 is implemented in the commercial CFD code, Ansys CFX. The CFD code solves for the momentum, continuity, enthalpy equations and for the additional transport equation of the reaction progress variable c. This equation is similar to eq. (1) with c as the transported variable instead of Y_n. At each iteration, the transported value of c is calculated, and the properties of the fluid and the chemical source term are retrieved from the CSP based database, via linear interpolation. The thermochemical mechanism used for the simulations carried out with Chemkin and CFX is the GRI 3.0 mechanism. The Chemkin final solution is found on a non-uniform grid of 516 points, and the Lewis number unity. The grid domain discretized in CFX is a uniform 70000 nodes mesh. The laminar flame speed, SL calculated with Chemkin Premix is assigned as the inlet boundary condition for the CFX simulation. In general the solutions obtained with CHEMKIN with all the detailed chemistry of GRI 3.0 compare very well with the predictions of CFX using tabulated chemistry and a single reaction progress variable. This is illustrated in figures 6 to 9 with CHEMKIN results in a solid line and CFX results in a dotted line. The profiles of Temperature, reactants NH3, O2 and product H2O is given in fig.4 (a). In the flame brush reactants are observed to be fully consumed and the temperature rises to about 2300 K and CFX and CHEMKIN have a very close match.
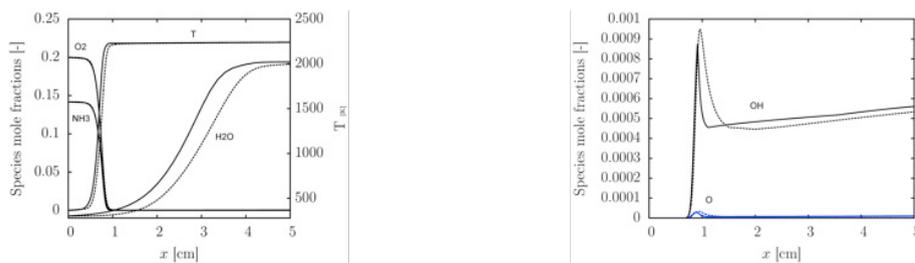
Fig. 4. (a) Profile of T,NH3,O2,H2O as function of distance; (b) Profile of OH, O as function of distance
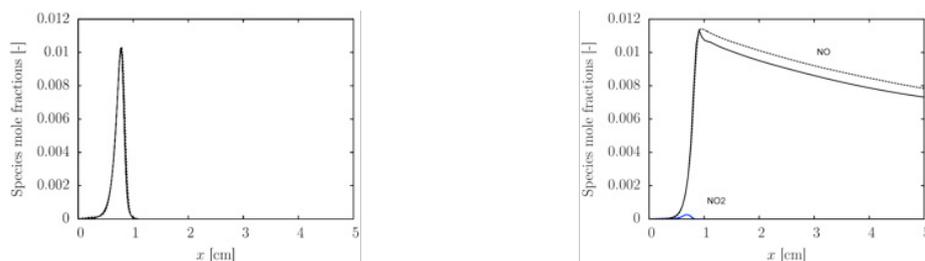
Fig. 5. (a) Profile of N2O as a function of distance; (b) Profile of NO, NO2 as function of distance.

On a much larger time scale the product H2O increases in the post flame zone to an equilibrium mole fraction of about 0.18. The profiles of CHEMKIN and CFX still compare qualitatively but CFX predicts with the tabulated chemistry a slightly delayed H2O production. The profiles of intermediate species OH and O are presented in fig 4(b). They both peak in the flame brush at x=1 cm. Subsequently O is completely consumed but OH reduces to about half the peak value in the post flame zone. CHEMKIN and tabulated chemistry compare very well. The reduction from peak value to post flame value is slightly delayed. For both the equilibrium has not been reached yet at x=5 cm. The profile of the slow species N2O is depicted in fig. 5(a). It is produced and peaking just ahead of the flame brush in the ignition zone and is downstream very fast consumed again. The comparison of tabulated chemistry and CHEMKIN is very good. Since one of the issues to be tackled in NH3 as a fuel for gas turbine engines is the emission of NO and NO2, the prediction of these toxic species is shown in fig. 5(b). It should be kept in mind that the time scale of these reactions is very different from the reactants. Hence a considerable deviation between tabulated chemistry and CHEMKIN should be expected: the former needs to handle the NOx chemistry in the tail of the reaction progress variable close to unity. Both NO and NO2 are observed to peak in the flame brush and are consumed again in the post flame zone. The NO2 concentrations are 2 orders of magnitude less then NO. The latter peaks at 1% and then reduces to 8000 PPM. The tabulated chemistry (CFXlinked) and CHEMKIN compare very well, with a slightly underpredicted reduction rate by the former.

Conclusion

The time scales of ammonia combustion are investigated and used to determine the slow species. The species which are in the range close to unity of the normalized time scale are the most suitable to represent the evolution of the reaction. These are O2, H2, N2O. A reaction progress variable is defined in two ways. The mathematical CSP procedure and the manual procedure using information on slow species are both used and results compared. With both progress variables a database with tabulated chemistry on basis of a single reaction progress variable is computed using laminar flame data. It appears that the results obtained with both methods compare very well. Both methods lead to a tabulated dependence of temperature that varies very linearly with reaction progress. The reaction progress variable source term as a function of reaction progress has a very similar shape and maximum obtained by the CSP and by the time scale method. It can be concluded that the ammonia chemistry does not show the intricate modeling complications as experienced with methane or ethanol and tabulated chemistry is very well possible. On basis of the CSP defined reaction progress variable a database of tabulated chemistry was created and linked to the CFD code CFX. A freely propagating laminar stoichiometric premixed atmospheric flame was simulated with full chemistry linked to CHEMKIN and with tabulated chemistry linked to CFX. Both simulations lead to almost identical results for the temperature and species profiles as a function of distance. The tabulated chemistry led to a slightly delayed production of H2O. The production of OH and NO up to their peak value compares very good, but the reduction afterwards to equilibrium values is predicted slightly delayed by the tabulated chemistry. The good comparison of NO is remarkable, as NO evolves at a much larger time scale that the species used for the reaction progress variable that were selected to predict the flame brush evolution. The results of the laminar flame simulation indicate very good possibilities for prediction of ammonia chemistry with tabulated chemistry in turbulent conditions.

References

[1] V.Fratalocchi, J.B.W.Kok, The CSP/PSR approach in reduced chemistry of premixed ethanol combustion, Comb. Science and Technology, http://dx.doi.org/10.1080/00102202.2017.1316266 ,2017.

[2] S Goevert, D Mira, JBW Kok, M Vazquez, and G Houzeaux. Turbulent combustion modelling of a confined premixed methane/air jet ame using tabulated chemistry. Energy Procedia, 66:313{316, 2015.

[3] DA Goussis, SH Lam, and PA Gnofio. Reduced and simplified chemical kinetics for air dissociation using computational singular perturbation. 1990.

[4] Robert J Kee, Fran M Rupley, and James A Miller. Chemkin-ii: A fortran chemical kinetics package for the analysis of gas-phase chemical kinetics. Technical report, Sandia National Labs., Livermore, CA (USA), 1989.

[5] SH Lam and DA Goussis. The csp method for simplifying kinetics. International Journal of Chemical Kinetics, 26(4):461{486, 1994.

[6] A Massias, D Diamantis, E Mastorakos, and DA Goussis. An algorithm for the construction of global reduced mechanisms with csp data. Combustion and Flame, 117(4):685{708, 1999.

[7] FA Williams. Combustion theory 2nd, 1985.